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INFRARED COATING STUDIES
FIRST QUARTER REPORT 1963

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INTRODUCTION

The first section of this report describes the enhancement
of reststrahleh high reflectance bands with thin films.
Both calculated and measured results are given for several
film combinations. The second section investigates the
possibility of replacing the metal films in metal-spacer-
metal filters with reststrahlen materials. The last sec-
tion extends some previous work done on the effect of
crystallite size on the infrared dispersion of LiF.

Section I - Enhanced Reststrahlen

For many years the reflectance of metals has been enhanced
with thin films. The design criteria used there may be
applied to the enhancement of reststrahlen bands. In
order to calculate the reflectance of such film combina-
tions it was necessary to write a new program for the IBM
1620 computer. This program allowed the use of dispersive
materials in thin film calculations. It is, however,
necessary to know for each material the dispersion param-
eters defined by the Drude formulas,

$$n^2 - k^2 - n_\infty^2 = \sum_j \frac{A_j(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \omega^2 q_j^2} \qquad (1)$$

$$2nk = \sum_j \frac{A_j \omega q_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 q_j^2} \qquad (2)$$

Unfortunately, the program does not handle dispersive sub-strates. This difficulty is overcome by using a thick opaque dispersive film as the effective substrate, but the approximation is good only in the region of opacity.

The dispersion parameters used in the calculations are listed in Table 1. The values used for CaF_2 and BaF_2 are those recently reported by Kaiser, Spitzer, Kaiser, and Howorth.[2] The parameters of LiF were determined under the previous contract.[3] It was, however, necessary to calculate the dispersion parameters of MgO. This was done in the standard way. The reflectance of massive MgO was fit by finding the appropriate parameters in the Drude dis-persion expressions and application of the Fresnel formula. Such a fit using only a single term in the summation is shown in Figure 3. The corresponding values of the index of refraction are also shown in this figure.

Infrared Dispersion Parameters of Several Ionic Crystals

	A_1	A_2	W_1	W_2	g_1	g_2	N
BaF_2	5.97×10^{27}	1.91×10^{26}	3.46×10^{13}	5.22×10^{13}	6.92×10^{11}	1.57×10^{13}	1.47
CaF_2	9.8×10^{27}	1.52×10^{27}	4.83×10^{13}	6.17×10^{13}	8.7×10^{11}	2.15×10^{13}	1.43
LiF	2.43×10^{28}	1.03×10^{27}	5.79×10^{13}	9.4×10^{13}	3.75×10^{12}	1.58×10^{13}	1.38
MgO	3.58×10^{28}	--	7.24×10^{13}	--	6.0×10^{12}	--	1.72

TABLE 1

A slight change in the notation used to describe the firm combinations is necessary. For example, consider the combination

$$G(.8D)(1.0H)(.8D)A \text{ at } \lambda = 20\mu$$

where D is a dispersive material and H has a real, non-dispersive index. The coefficient of D is h/λ where h is the physical thickness of the layer and λ is, as indicated, 20μ. The coefficient of H is the number of quarter waves at λ equal to 20μ, i.e., $4nh/\lambda$.

The dotted lines in Figures 1, 2, 4, and 5 show the calculated reflectance of a single layer of germanium on CaF_2, BaF_2, MgO, and LiF respectively. The thickness of the germanium film was chosen to give constructive interference at the wavelength indicated at the top of the figure. The reflectance is significantly enhanced in all cases. It is perhaps somewhat surprising that the region of enhancement is so broad. The reflectance does not drop until the immediate neighborhood of destructive interference is reached. Consider, for example, the minima in the reflectance of enhanced LiF (Figure 5). At the enhancing wavelength, 20 microns, the germanium film must be slightly thicker than a quarter wave to compensate for the negative phase shift at the Ge-LiF interface. At approximately 13 microns the Ge-LiF interface phase shift is zero and the film is a half wave thick, resulting in no change in refectance. At 33 microns the positive phase shift due to the

film thickness is exactly equal to the negative phase shift at the Ge-LiF interface, resulting in destructive interference.

Measurements of reststrahlen enhanced with a single layer of germanium proved somewhat disappointing. The reflectance was down considerably from the calculated values for the two materials coated, CaF_2 and LiF (Figs. 1, 5). This was undoubtedly due to absorption in the germanium film. This absorption was dependent on the evaporating conditions. Slow rates of evaporation and high substrate temperatures will probably produce films with fewer defects and, therefore, with fewer free electrons to absorb energy. No systematic investigation was made of this germanium absorption.

Calculations were made of a two layer enhancement of the reststrahlen of LiF. The low index material used was $PbCl_2$; the high index material, germanium. Figure 6 shows that this construction brought the reflectance up to 98%. The $PbCl_2$, incidently, antireflects the rear surface of the germanium film at about 10 microns. This construction was attempted several times experimentally. Although the resulting enhancement varied considerably from sample to sample, it was possible to closely approach the calculated values (Fig. 6).

A serious disadvantage is introduced if these high reflectance bands are to be used for filtering. Normally

the reflectance is only a few percent on the short wave-
length side of the band. After enhancement with germanium
it is seen that the relatively good background is destroy-
ed. The background is lowered, though, on the immediate
long wavelength side of the band. In an effort to improve
the short wavelength background a third layer was added to
the combination. The thickness of this layer was chosen
to anti-reflect the first surface of the germanium film at
11 microns. Figure 7 shows the calculated and measured
results. The peak at 11 microns was successfully anti-
reflected, and the short wavelength side of the high re-
flectance band was lowered slightly. Normally multiple
reflection techniques are used in reststrahlen filtering.
Figure 8, for example, shows the result after three re-
flections off LiF. The short wavelength background is
excellent, .0001%. The long wavelength background is
rather poor and the reflectance band averages only 55%.
The result after two reflections off LiF with a two layer
enhancement and one reflection off unenhanced LiF is also
shown in Figure 8. Although the excellent short wave-
length background has been destroyed, the average value in
the high reflectance band is raised to 75% and the long
wavelength background is significantly lowered.

Section II - Reststrahlen Interference Filters

The usefulness of a metal in a metal-spacer-metal inter-
ference filter is determined by the ratio k/n, where k is

the imaginery part of the index and n is the real part.
For the ideal metal (n→o) this ratio is infinity. For
aluminum in the visible the ratio is about 10. This ratio
of 10, in fact, sets the limit for usable metals in inter-
ference filters. As wavelength increases, k/n approached
1 for all metals. At 20 microns there are no known metals
suitable for use in interference filters. In the region
of reststrahlen dispersion the ratio of k/n for a LiF film
evaporated onto a substrate at $300^{\circ}C$ is between 5 and 10.
This borderline ratio suggest the possibility of replacing
the metals with reststrahlen materials. Using the com-
puter program mentioned in Section I it was possible to
calculate the transmission of a filter so constructed.

The dispersion parameters of the LiF film were calculated
in a previous report[3] The spacer layer was assumed to
have an index corresponding to that of $PbCl_2$, 1.8. The
substrate was KBr with an index of 1.46. Figure 9 shows
that the calculated transmission of 3 and 5 layer first
order filters peaked at 23 microns. Figure 10 shows the
transmission of the same combinations with the spacer
layer thickness chosen for third order interference.
Filters with such low peak to background ratios are not
desirable, particularly in the infrared where it is neces-
sary to deal with very low intensities.

The problem of improving the filter might be approached
in the following manner. k/n for a thin film of LiF is

considerably lower than that for a single crystal of LiF. This is thought to be due to a crystallite size effect. If the indices of the film could be made to more closely approximate those of a single crystal, a little more interesting filter could be fabricated. There is, of course, also the possibility of finding a reststrahlen material more suitable than LiF.

Section III - Effect of Crystallite size on the Infrared Dispersion of LiF - Part II

A study of the effect of crystallite size on the infrared dispersion of LiF was reported in the First Quarterly Report of 1962. In this study it was necessary to make the films opaque in the region of interest because computational facilities were not available for interference effects in dispersive thin films. Now that such facilities are available the results of previous work may be tested with the thinner films.

A brief review of the previous work might be helpful. Six micron thick films of LiF were evaporated onto glass. The infrared reflectance was measured at normal incidence. This empirical reflectance curve was fit with a theoretical curve obtained by finding the appropriate parameters in the Drude dispersion expression and application of the Fresnel formula. The size of the crystallites composing the film were increased by increasing the temperature of

the substrate during deposition. The following correlation was found to exist between crystallite size and Drude dispersion parameters. As the crystallites became smaller;

a) the damping (g_1, g_2) in both terms increased,

b) the strength of the main resonance (A_2) became slightly smaller,

c) the strength of the secondary resonance (A_1) rapidly increased.

The crystallite size of an evaporated film is dependent not only on substrate temperature, but also the thickness of the film. In this experiment the crystallite size was varied by varying the film thickness. The crystallite size of the films has been determined using electron microscopy. The technique used for making carbon replicas of the surface is exactly the same as described in the Second Quarter Report, 1962. Figure 11 shows a series of electron micrographs of these replicas for several film thicknesses. The increase in crystallite size with increasingly thick films is evident. Since all films were evaporated onto a substrate at room temperature, the surface structure is not smoothed out as it was at higher temperatures in the previous experiment. If it is assumed that the average dimension of an exposed face is a measure of crystallite size then Figure 12 shows the dependence of size on film thickness. This dependence appears to be linear for relatively thin films. The growth of the crystallites appears to saturate after they reach 4000-

5000 A in size.

Thin films of LiF were evaporated onto KRS-5. The trans-
mission of these samples was measured, and the appropriate
corrections were made for the second surface reflection of
the substrate. The corrected transmission of samples of
several different thicknesses is shown in Figure 13.
Using the computer program mentioned above an attempt was
made to fit these transmission measurements by a suitable
choice of the dispersion parameters in a two term Drude
expression. The thicknesses of these films were known
from transmission measurements made in the near infrared.
It is not surprising that the parameters determined for
single crystal LiF[3] do not result in a fit of the trans-
mission curves of these small crystal films (Fig. 14).

Figure 15 shows the transmission calculated using the
dispersion parameters obtained from the fit of the reflect-
ance of the 6 micron thick films evaporated onto a sub-
strate at room temperature.[3] These curves should corres-
pond to the transmission of films with 5000 A crystallites.
Although the size of the crystallites in the films used
here is smaller, it is perhaps surprising that these
curves fit the data so poorly. A fairly good fit to the
transmission data is made when the parameters indicated in
Figure 16 are used. This presents an even more difficult
problem. The correlations found previously between crys-
tallite size and Drude dispersion parameters, when extra-

polated to smaller crystallites, should yield fairly good parameters. The parameters used in Figure 16 do not follow this trend. Moreover, the parameters used to fit the transmission data do not result in a fit of the previous reflectance data (Fig. 17). They also give a long wavelength index of refraction almost twice as large as it should be.

An explanation for all these difficulties has not been found. It is possible that the Drude dispersion formula is not applicable to this problem. Born and Huang have developed a dispersion expression based on a quantum mechanical pertubation calculation (eq. 2,3).

$$n^2 - k^2 - n_\infty^2 = \left(\frac{A}{\omega_0 + \omega}\right) \frac{\omega_0 - \omega + q^2/2\omega_0}{(\omega_0 - \omega)^2 + q^2} \tag{3}$$

$$2nk = \left(\frac{Aq}{2\omega_0}\right) \frac{1}{(\omega_0 - \omega)^2 + q^2} \tag{4}$$

In these equations g is a function of w. g(w) may be calculated if the lattice vibrational spectrum is known. This is a considerable improvement over the g in the Drude expression, which is just an arbitrary velocity proportional damping constant with little physical significance. It can be noticed that both sets of expressions have the same limit when g goes to zero. This might explain why the Drude formula is so good for single crystal LiF. For thin films, though, it appears that g increases considerably, and it may be necessary to use the more exact Born-Huang expression.
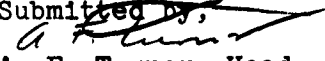
ACKNOWLEDGEMENTS

REFERENCES

1) Bilz, Genzel, and Happ, "Zur Ultrarotdispersion der AlkaliHalogenide," <u>Z. Physik</u>, Vol. 160, 1960, P. 535.

2) Kaiser, Spitzer, Kaiser, and Howarth, "Infrared Properties of CaF_2 SrF_2, and BaF_2," Phys. Rev., Vol. 127, 1962, p. 1950.

3) Martin, First Quarter Report to Fort Belvoir, Contract DA-44-009-ENG-4954, 1962.

4)   , Second Quarter Report to Fort Belvoir, Contract DA-44-009-ENG-4954, 1962.

This report was prepared by T. P. Martin

Submitted by;

A. F. Turner, Head
Optical Physics, Research
   and Development

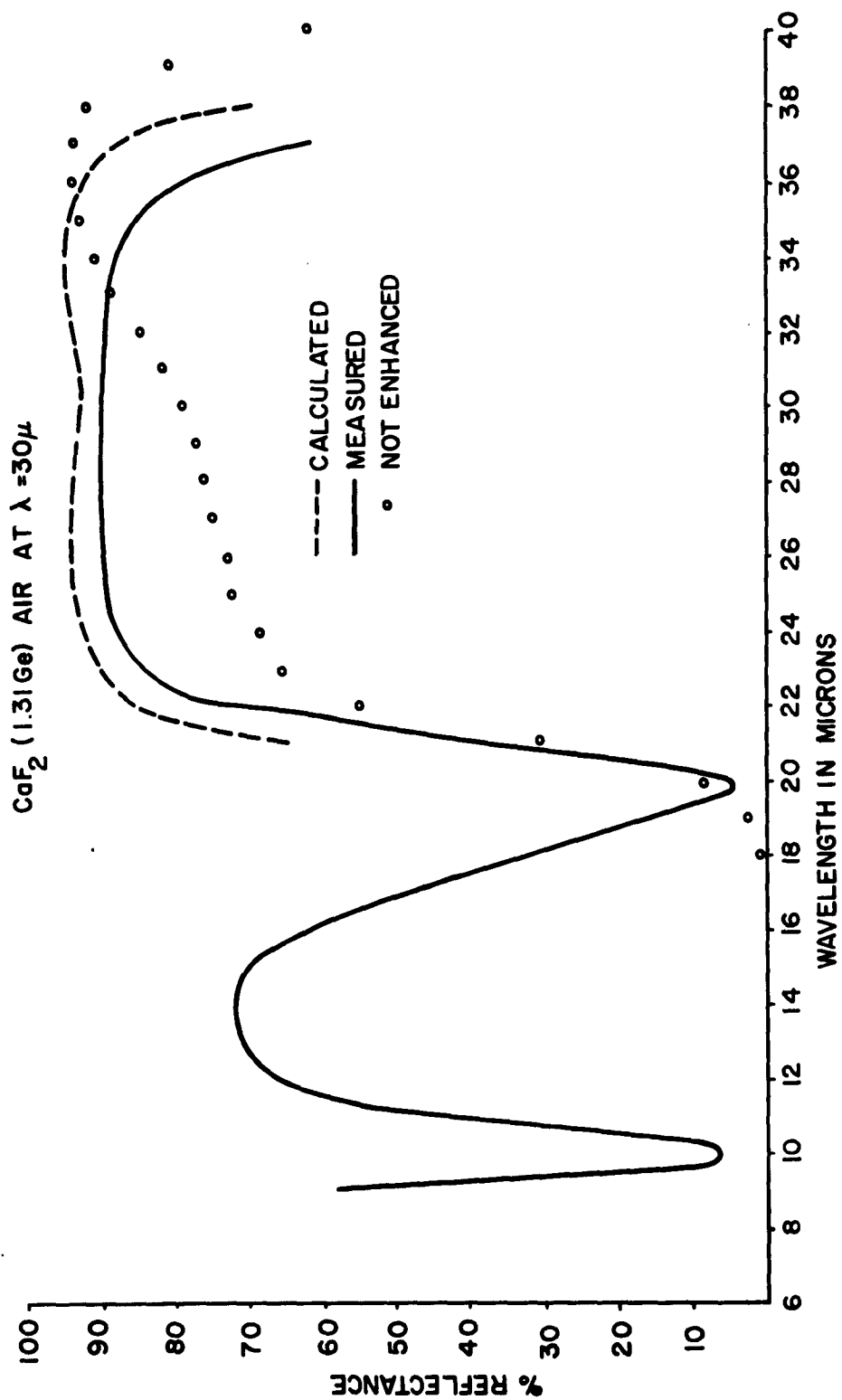SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF CaF_2

CaF_2 (1.31 Ge) AIR AT $\lambda = 30\mu$

---- CALCULATED
——— MEASURED
∘ NOT ENHANCED

% REFLECTANCE

WAVELENGTH IN MICRONS

FIG. 1

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF BaF₂

BaF₂ (1.21 Ge) AIR AT λ = 42μ

— — — CALCULATED

∘ NOT ENHANCED

% REFLECTANCE

WAVELENGTH IN MICRONS
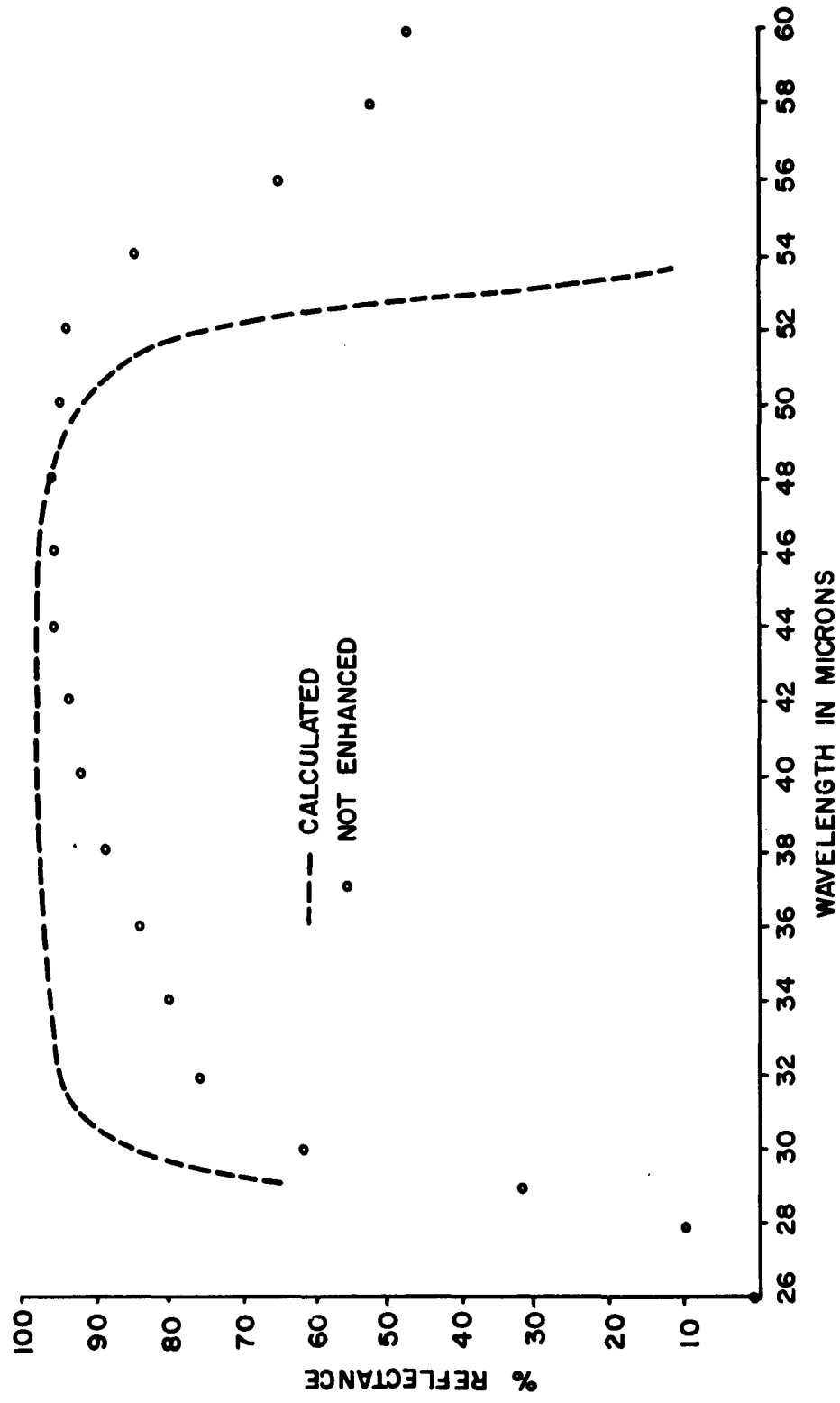
FIG. 2

REFLECTANCE AND DISPERSION OF MgO IN THE RESTSTRAHLEN REGION

o MEASURED REFLECTANCE
— CALCULATED REFLECTANCE FIT
--- INDEX OF REFRACTION

INDEX OF REFRACTION

% REFLECTANCE

WAVELENGTH IN MICRONS
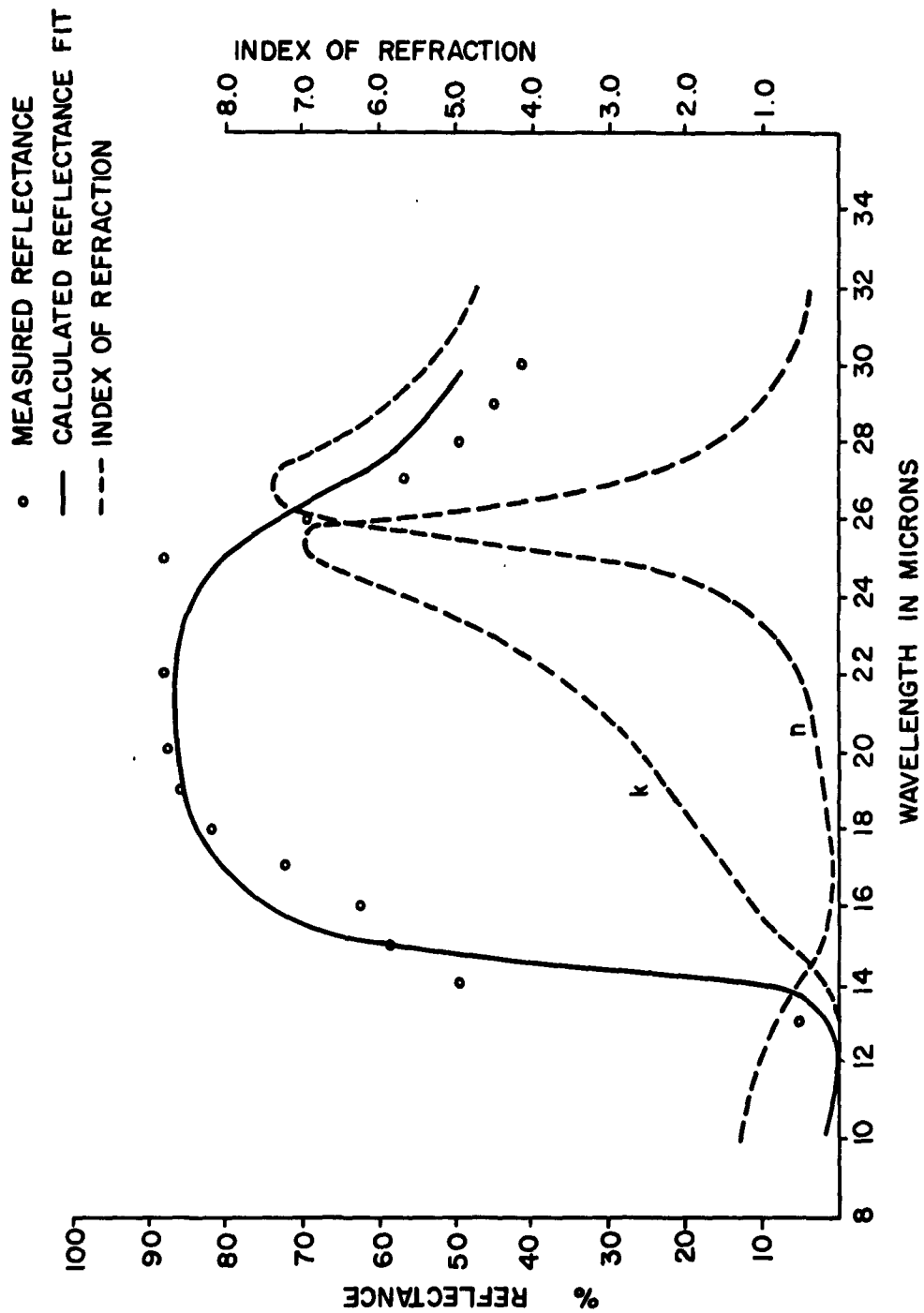
FIG. 3

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF MgO

MgO (1.29 Ge) AIR AT $\lambda = 18\mu$

— — — CALCULATED
o   NOT ENHANCED

% REFLECTANCE

WAVELENGTH IN MICRONS
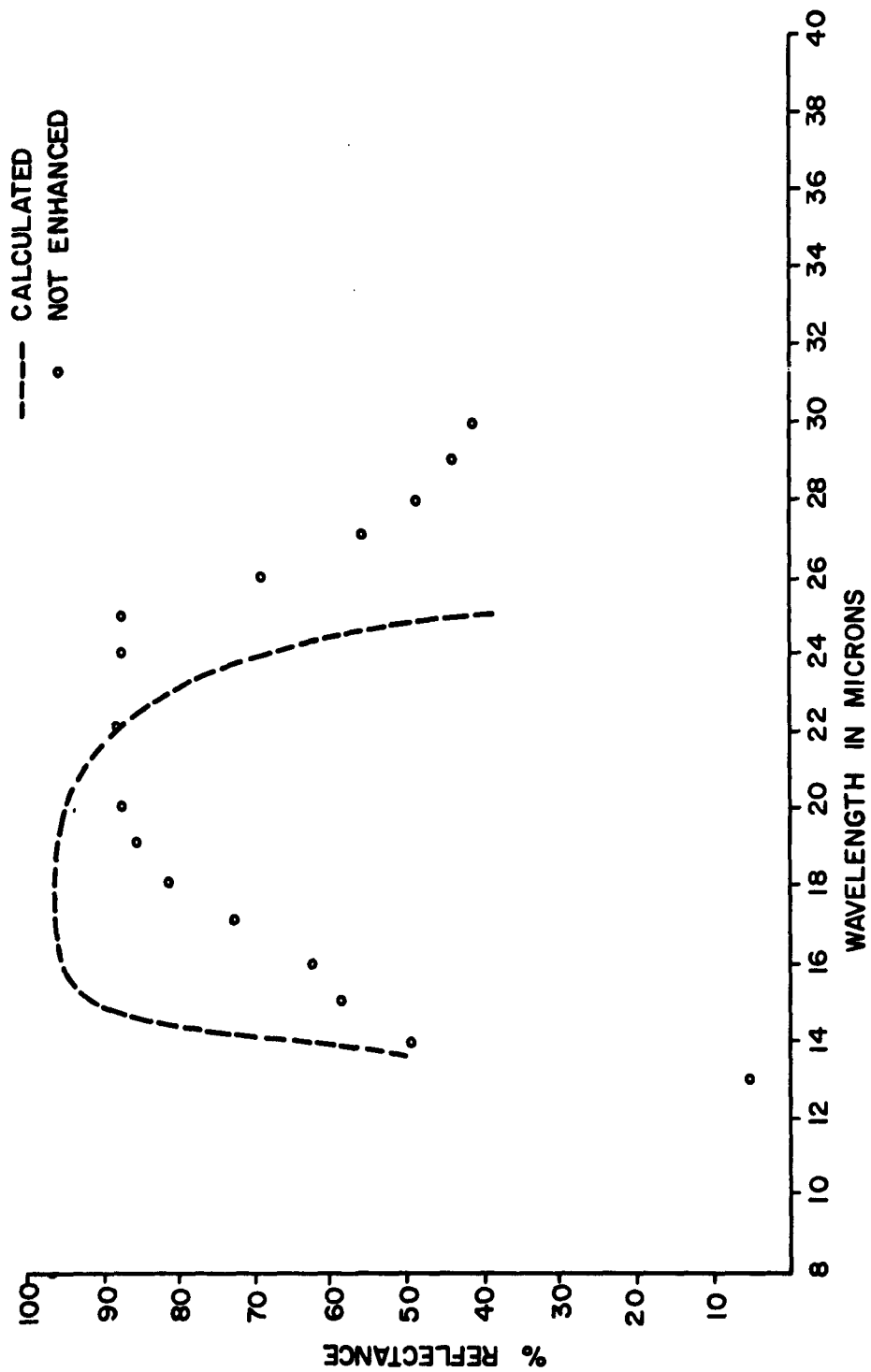
FIG. 4

SINGLE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF LiF

LiF (1.26Ge) AIR AT λ = 20

- - - - CALCULATED
———— MEASURED
o   NOT ENHANCED

% REFLECTANCE

WAVELENGTH IN MICRONS
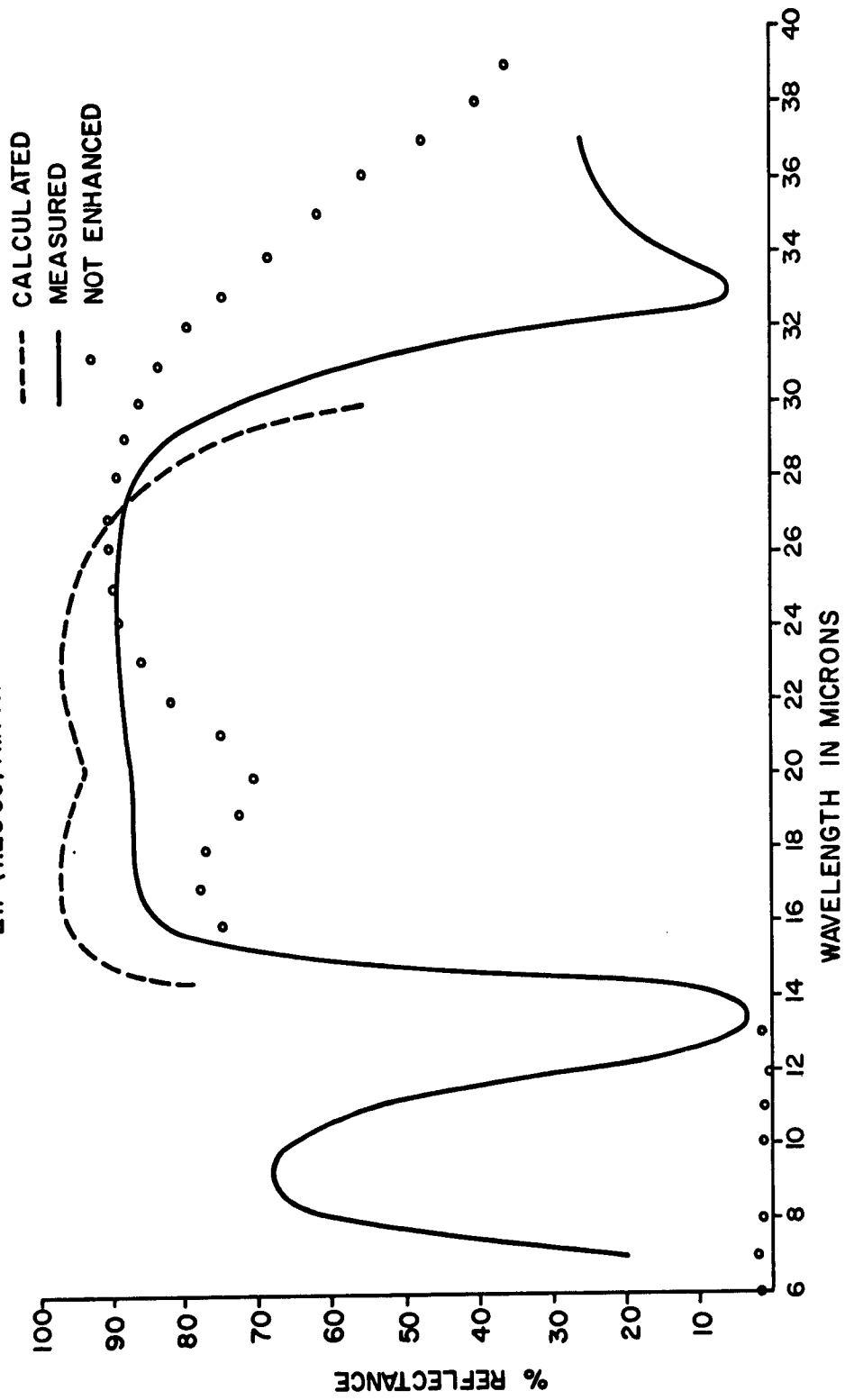
FIG. 5

TWO LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF LiF

LiF (.47 Pb Cl$_2$)(1.0 Ge) AIR AT λ = 20

- - - CALCULATED
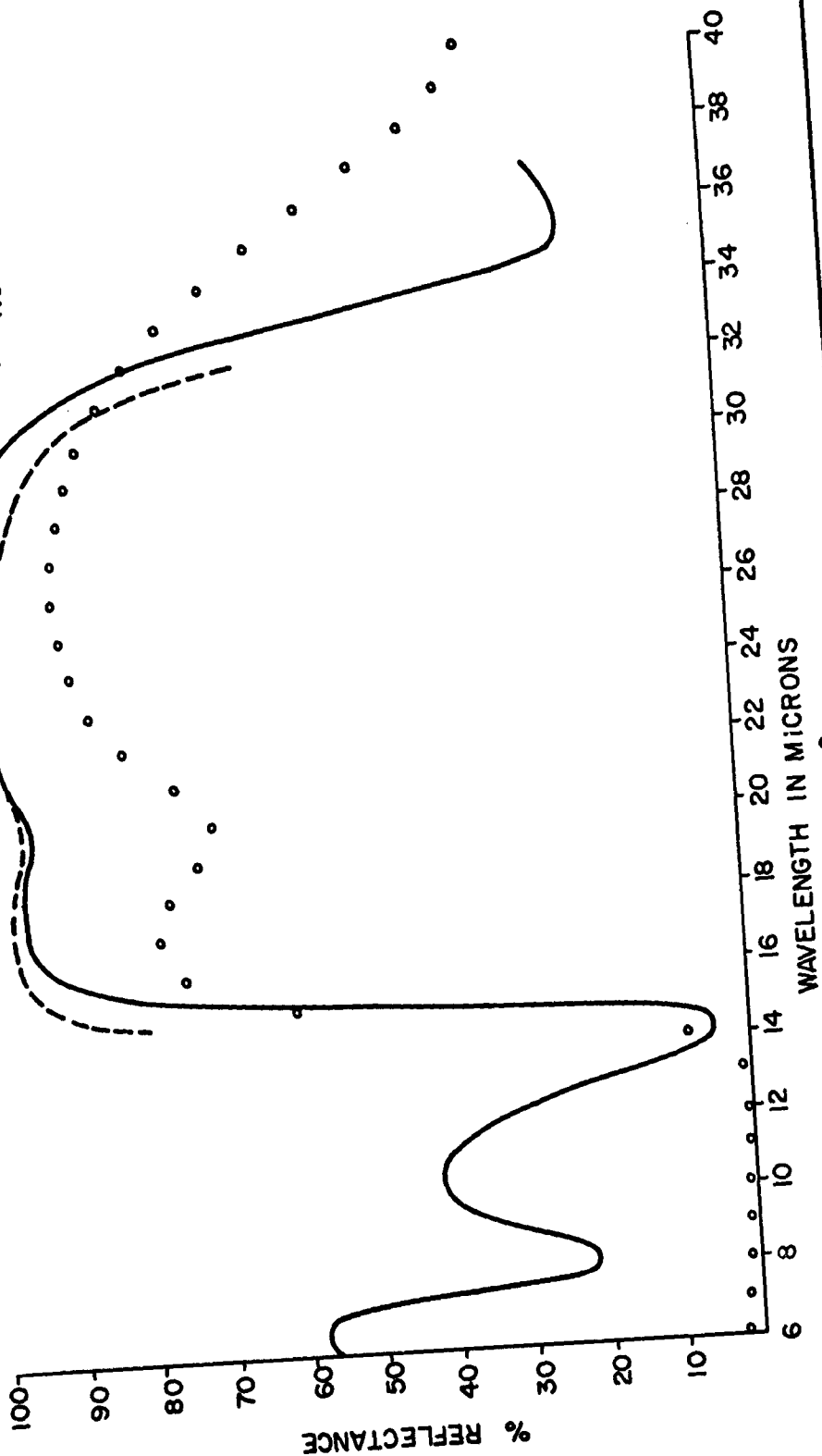——— MEASURED
○ NOT ENHANCED

% REFLECTANCE

WAVELENGTH IN MiCRONS

FIG. 6

THREE LAYER ENHANCEMENT OF THE RESTSTRAHLEN OF LiF

LiF (.47 PbCl$_2$)(1.0Ge)(.55 PbCl$_2$)AIR AT λ =20

--- CALCULATED
— MEASURED
○ NOT ENHANCED

% REFLECTANCE

WAVELENGTH IN MICRONS
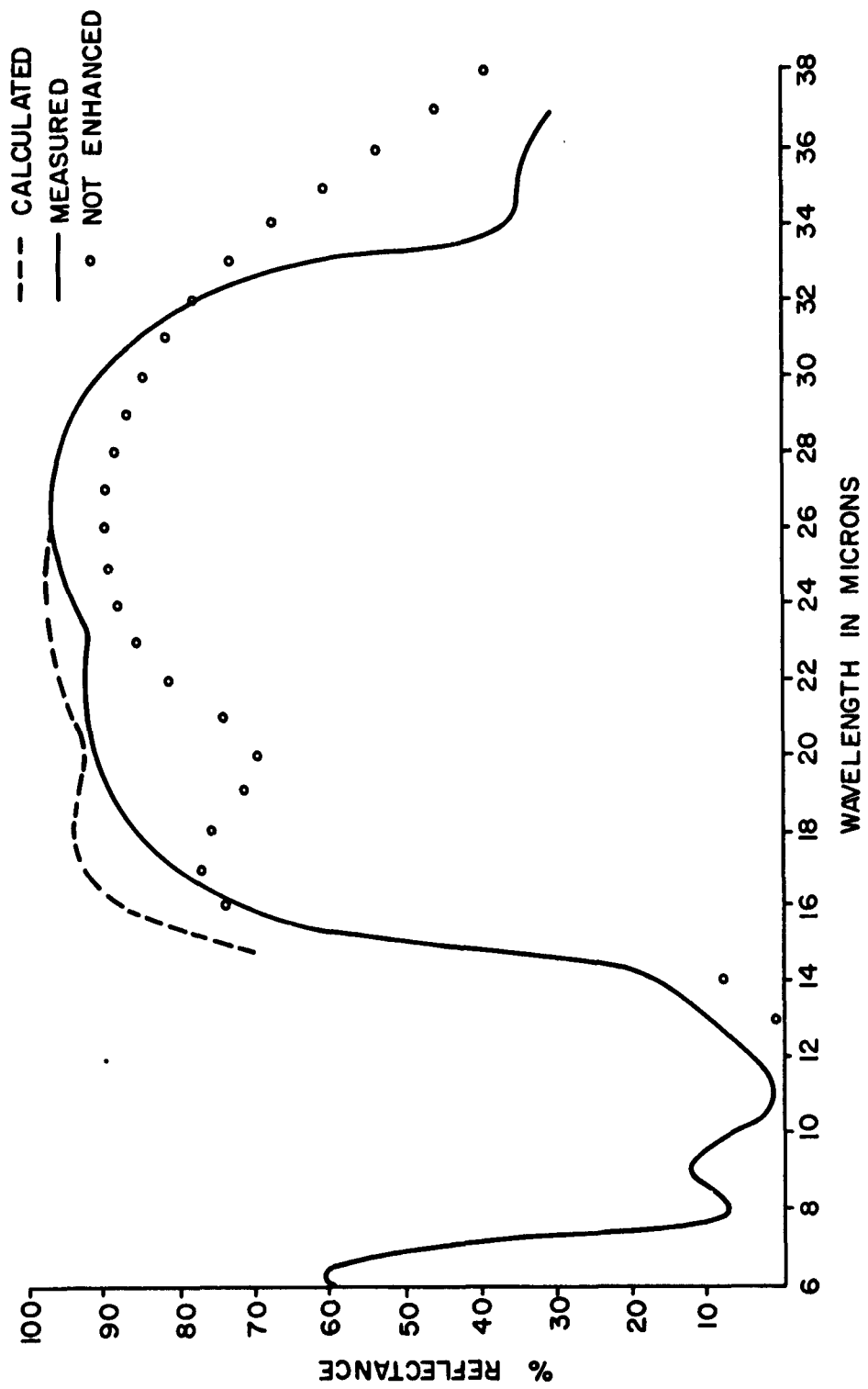
FIG. 7

RESTSTRAHLEN FILTERING WITH ENHANCED LiF

$(R_{LiF})(R_{ENLiF})^2$

$(R_{LiF})^3$

(R_{LiF})

% REFLECTANCE

WAVELENGTH IN MICRONS

FIG. 8

CALCULATED TRANSMISSION OF A FIRST ORDER
RESTSTRAHLEN INTERFERENCE FILTER

KBr(.098LiF)(1.1 PbCl$_2$)(.098LiF) AIR

KBr(.098LiF)(1.1PbCl$_2$)(.196 LiF)(1.1PbCl$_2$)(.098LiF) AIR at 23μ

% TRANSMISSION

WAVELENGTH IN MICRONS

FIG. 9

CALCULATED TRANSMISSION OF A THIRD ORDER
RESTSTRAHLEN INTERFERENCE FILTER

KBr(.098 LiF)(5.1 PbCl$_2$)(.098 LiF) AIR

KBr(.098LiF)(5.1PbCl$_2$)(.196LiF)(5.1PbCl$_2$)(.098LiF) AIR at 23μ

% TRANSMISSION

WAVELENGTH IN MICRONS
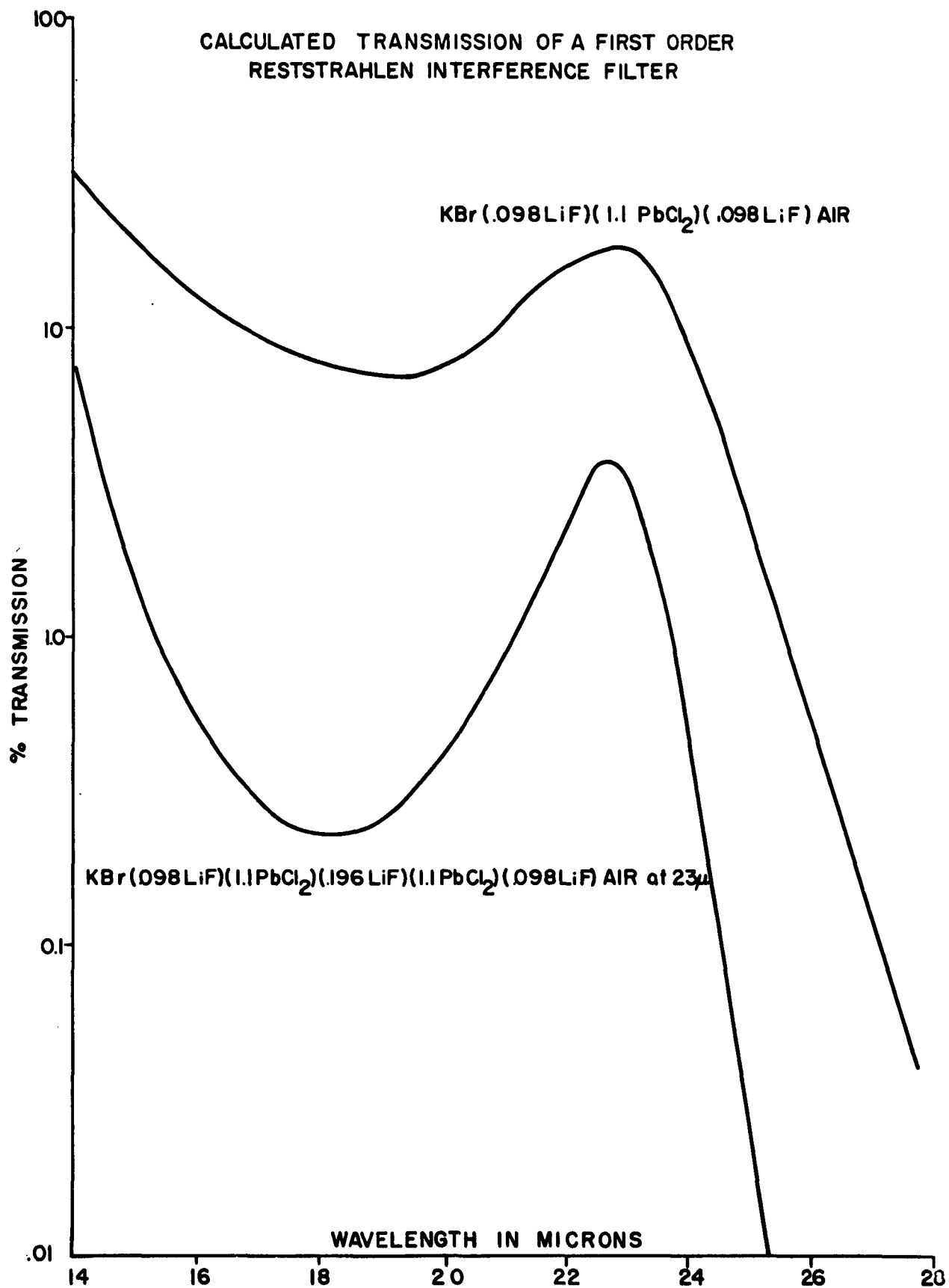
FIG. 10

ELECTRON MICROGRAPHS OF LiF THIN FILMS
OF INDICATED THICKNESS

.25μ   .5μ   1μ   2μ
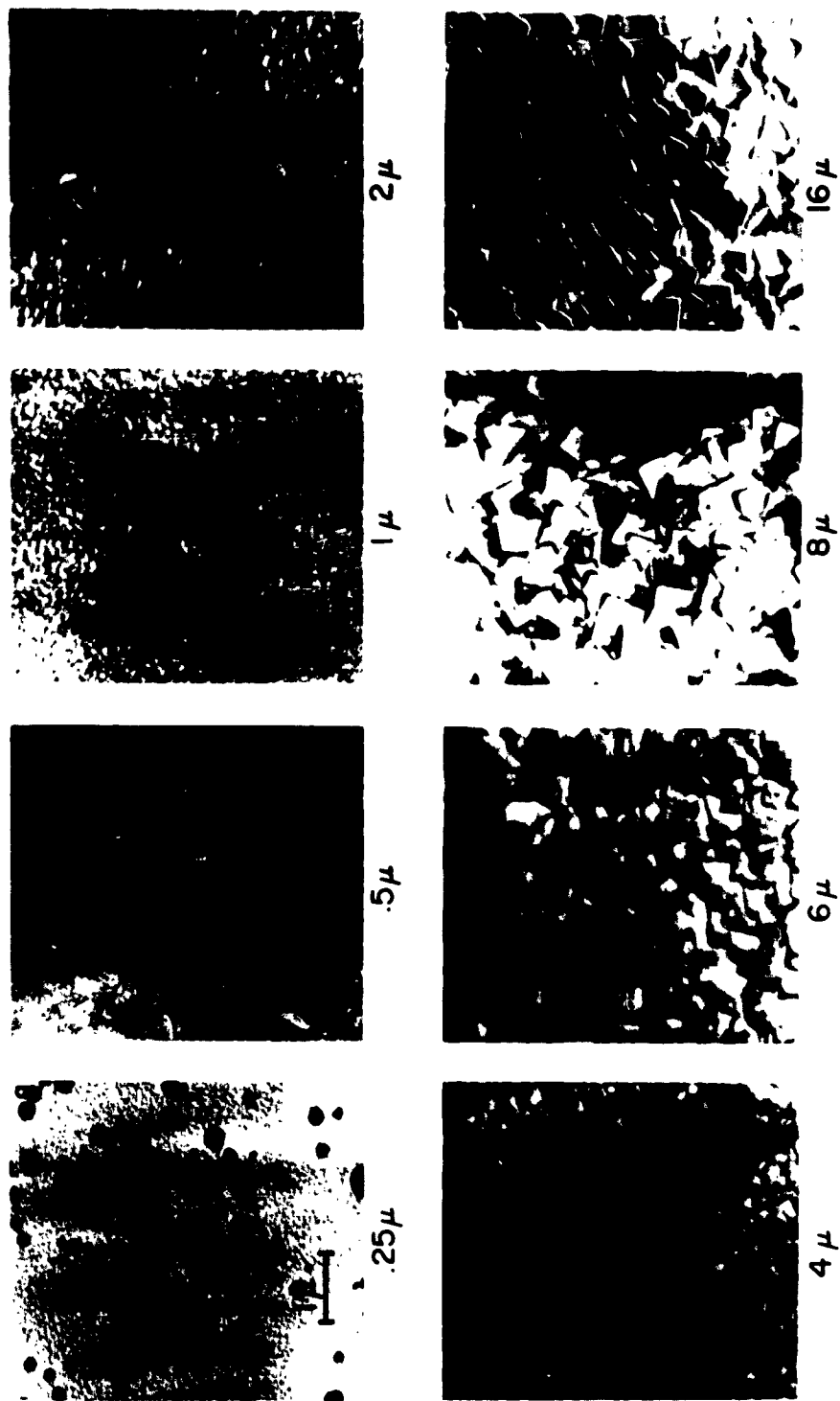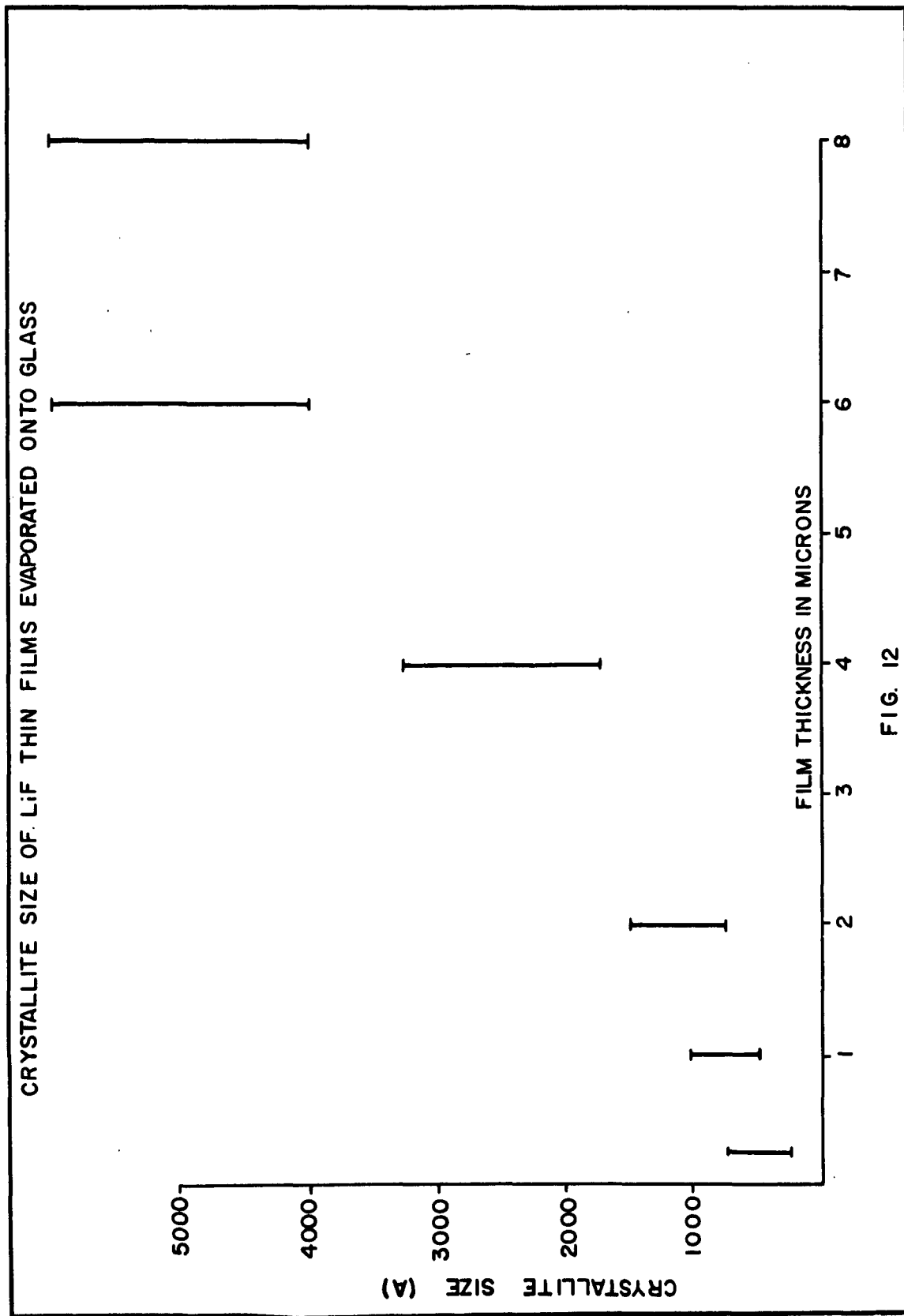
4μ   6μ   8μ   16μ

FIGURE II

CRYSTALLITE SIZE OF LiF THIN FILMS EVAPORATED ONTO GLASS

FILM THICKNESS IN MICRONS

FIG. 12

CRYSTALLITE SIZE (Å)

CORRECTED TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

.22 μ
.32 μ
.72 μ
1.44 μ
3.00 μ

WAVELENGTH IN MICRONS

FIG. 13

% TRANSMISSION

CALCULATED TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

$A_1 = 1.03 \times 10^{27}$
$A_2 = 24.3 \times 10^{27}$
$g_1 = 1.58 \times 10^{13}$
$g_2 = 4.25 \times 10^{12}$
$\omega_1 = 9.4 \times 10^{13}$
$\omega_2 = 5.79 \times 10^{13}$
$n_\infty = 1.38$

.18μ
.36μ
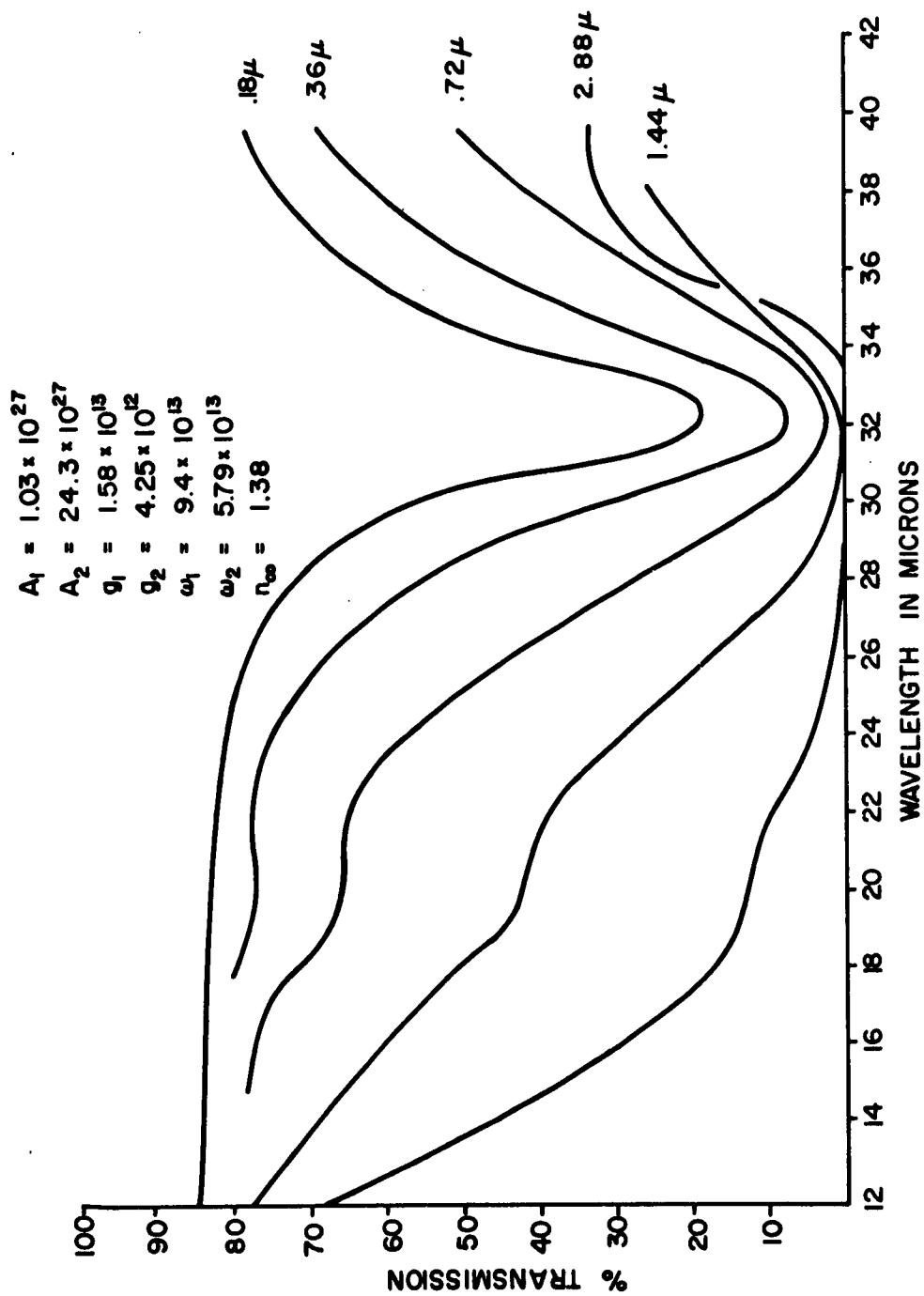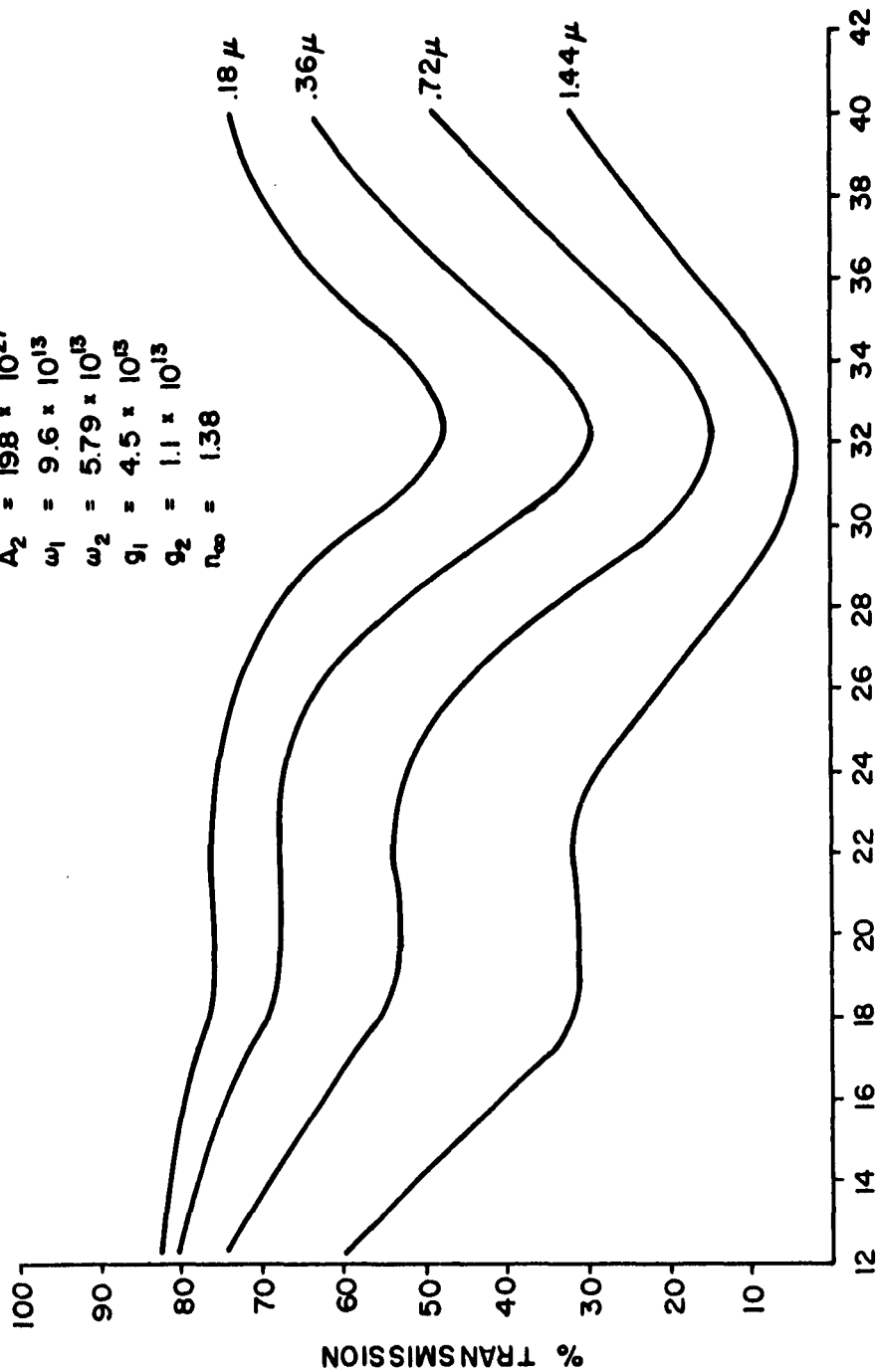.72μ
2.88μ
1.44μ
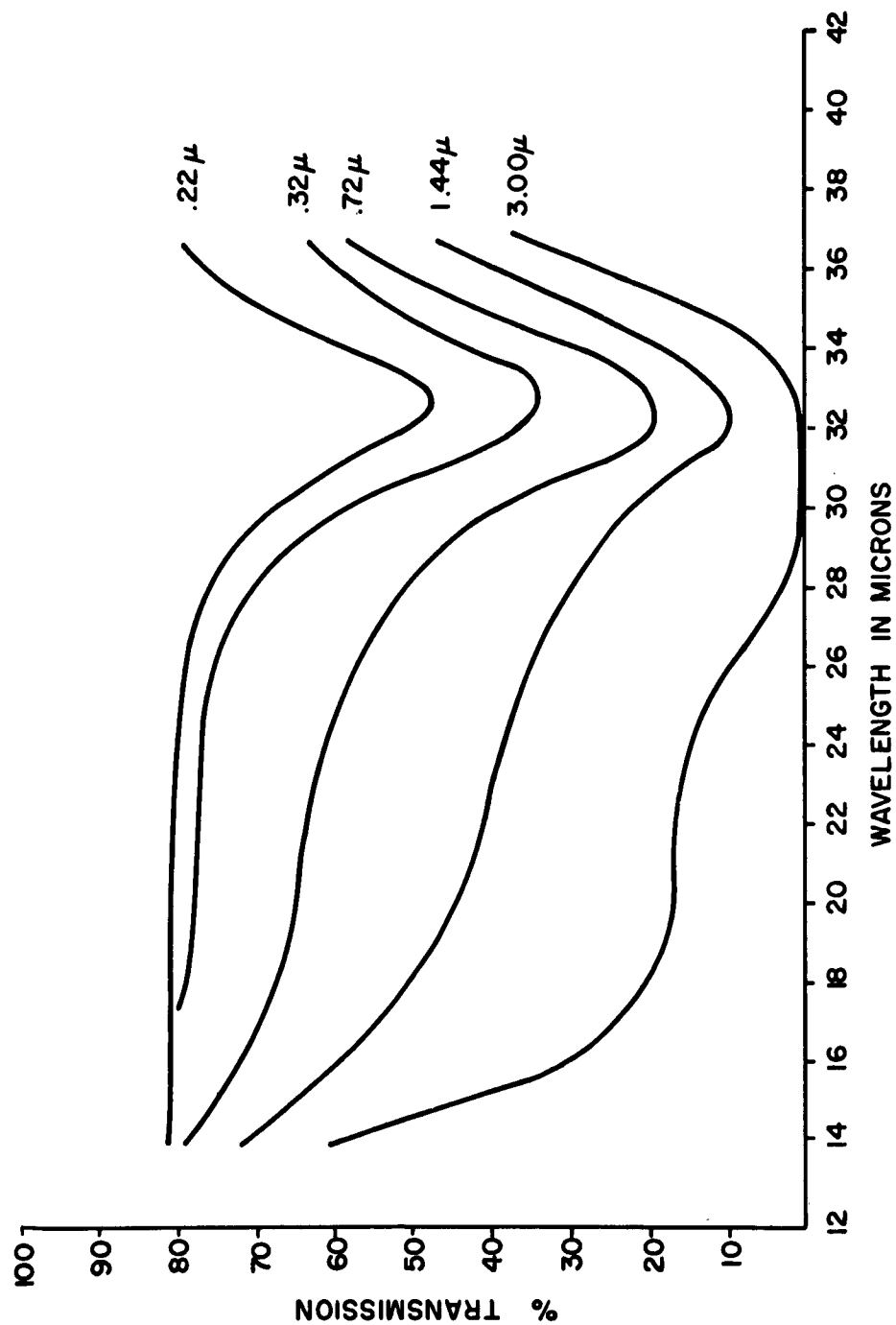
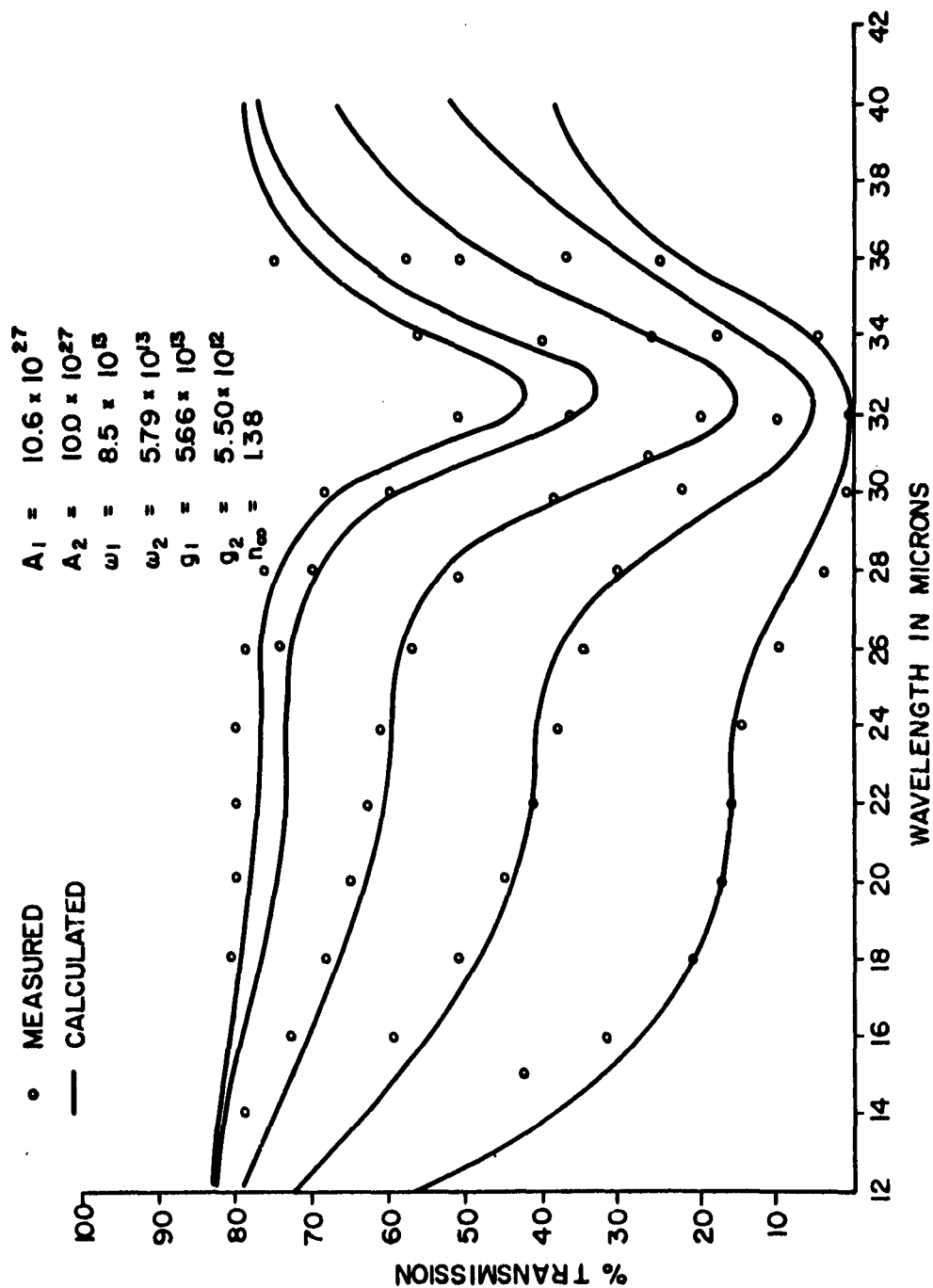WAVELENGTH IN MICRONS

FIG. 14

% TRANSMISSION

CALCULATED TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

$A_1 = 10.6 \times 10^{27}$
$A_2 = 198 \times 10^{27}$
$\omega_1 = 9.6 \times 10^{13}$
$\omega_2 = 5.79 \times 10^{13}$
$g_1 = 4.5 \times 10^{13}$
$g_2 = 1.1 \times 10^{13}$
$n_\infty = 1.38$

.18 μ
.36 μ
.72 μ
1.44 μ

WAVELENGTH IN MICRONS
FIG. 15

% TRANSMISSION

TRANSMISSION OF LiF THIN FILMS EVAPORATED ONTO KRS-5

○ MEASURED

— CALCULATED

$A_1 = 10.6 \times 10^{27}$
$A_2 = 100 \times 10^{27}$
$\omega_1 = 8.5 \times 10^{13}$
$\omega_2 = 5.79 \times 10^{13}$
$g_1 = 5.66 \times 10^{13}$
$g_2 = 5.50 \times 10^{12}$
$n_\infty = 1.38$

% TRANSMISSION

WAVELENGTH IN MICRONS

FIG. 16

RESTSTRAHLEN OF A LiF FILM EVAPORATED ONTO GLASS AT 35°C

THICKNESS—6μ

○ MEASURED
— CALCULATED

% REFLECTANCE

WAVELENGTH IN MICRONS
FIG. 17